

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

ATTORNEY'S DOCKET NUMBER

029430-507

U S APPLICATION NO (If known, see 37 C.F.R. 1.5)

Unassigned **10/089302**INTERNATIONAL APPLICATION NO.  
PCT/JP00/06635INTERNATIONAL FILING DATE  
September 27, 2000PRIORITY DATE CLAIMED  
September 29, 1999

## TITLE OF INVENTION

CATALYST FOR DECOMPOSING ORGANIC HARMFUL SUBSTANCES AND METHOD FOR DECOMPOSING  
ORGANIC HALIDES BY USE THEREOF

## APPLICANT(S) FOR DO/EO/US

Isao TAKASU et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

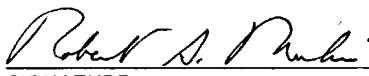
1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

**Items 11 to 20 below concern document(s) or information included:**

11. ☒ An Information Disclosure Statement under 37 C.F.R. § 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 C.F.R. § 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information: Form PCT/IB/304; Form PCT/IB/308; (copy) front page International Publication No. WO 01/23086 A1; Form PCT/IB.338; Form PCT/IPEA/409; Form PCT/ISA/210 (second sheet); Information Disclosure Statement Transmittal Letter; Form PTO-1449

**21839**

1015-Rec'd PCT/PTO 29 MAR 2002

U.S. APPLICATION NO. (If known, fee of 37 C.F.R. § 1.51) Unassigned <b>10/089302</b>		INTERNATIONAL APPLICATION NO. PCT/JP00/06635		ATTORNEY'S DOCKET NUMBER 029430-507	
21. <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS	PTO USE ONLY
<b>Basic National Fee (37 C.F.R. § 1.492(a)(1)-(5)):</b> Neither international preliminary examination fee (37 C.F.R. § 1.482) nor international search fee (37 C.F.R. § 1.445(a)(2)) paid to U.S. PATENT AND TRADEMARK OFFICE and International Search Report not prepared by the EPO or JPO . . . . . \$1,040.00 (960) International preliminary examination fee (37 C.F.R. § 1.482) not paid to U.S. PATENT AND TRADEMARK OFFICE but International Search Report prepared by the EPO or JPO . . . . . \$890.00 (970) International preliminary examination fee (37 C.F.R. § 1.482) not paid to U.S. PATENT AND TRADEMARK OFFICE but international search fee (37 C.F.R. § 1.445(a)(2)) paid to U.S. PATENT AND TRADEMARK OFFICE . . . . . \$740.00 (958) International preliminary examination fee (37 C.F.R. § 1.482) paid to U.S. PATENT AND TRADEMARK OFFICE but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . \$710.00 (956) International preliminary examination fee (37 C.F.R. § 1.482) paid to U.S. PATENT AND TRADEMARK OFFICE and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . \$100.00 (962)					
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				\$ 890.00	
Surcharge of \$130.00 (154) for furnishing the oath or declaration later than months from the earliest claimed priority date (37 C.F.R. § 1.492(e)). 20 <input type="checkbox"/> 30 <input type="checkbox"/>				\$	
Claims	Number Filed	Number Extra	Rate		
Total Claims	11 -20 =	0	X\$18.00 (966)	\$ 0.00	
Independent Claims	1 -3 =	0	X\$84.00 (964)	\$ 0.00	
Multiple dependent claim(s) (if applicable)			+ \$280.00 (968)	\$	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$ 890.00	
Reduction for ½ for filing by small entity, if applicable (see below).				+	\$ -
<b>SUBTOTAL =</b>				\$ 890.00	
Processing fee of \$130.00 (156) for furnishing the English translation later than months from the earliest claimed priority date (37 C.F.R. § 1.492(f)). 20 <input type="checkbox"/> 30 <input type="checkbox"/>				\$	
<b>TOTAL NATIONAL FEE =</b>				\$ 890.00	
Fee for recording the enclosed assignment (37 C.F.R. § 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 C.F.R. § 3.28, 3.31). \$40.00 (581) per property				+	\$ 40.00
<b>TOTAL FEES ENCLOSED =</b>				\$ 930.00	
				<b>Amount to be refunded:</b>	\$
				<b>charged:</b>	\$
a. <input type="checkbox"/> Small entity status is hereby claimed. b. <input checked="" type="checkbox"/> A check in the amount of \$ <u>930.00</u> to cover the above fees is enclosed. c. <input type="checkbox"/> Please charge my Deposit Account No. <u>02-4800</u> in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. d. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>02-4800</u> . A duplicate copy of this sheet is enclosed.					
<b>NOTE: Where an appropriate time limit under 37 C.F.R. § 1.494 or 1.495 has not been met, a petition to revive (37 C.F.R. § 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b>					
SEND ALL CORRESPONDENCE TO:					
Robert G. Mukai BURNS, DOANE, SWECKER & MATHIS, L.L.P. P.O. Box 1404 Alexandria, Virginia 22313-1404 (703) 836-6620			<div style="text-align: center;">               SIGNATURE              Robert G. Mukai              NAME              28,531              REGISTRATION NUMBER           </div> <div style="text-align: right;">             March 29, 2002              DATE           </div>		

Attorney's Docket No. 029430-507

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of	)	
	)	
Isao TAKASU et al.	)	Group Art Unit: Unassigned
	)	
Application No.: New U.S. National Phase	)	Examiner: Unassigned
Application of	)	
PCT/JP00/06635,	)	
filed September 27, 2000	)	
	)	
Filed: March 29, 2002	)	
	)	
For: CATALYST FOR DECOMPOSING	)	
ORGANIC HARMFUL	)	
SUBSTANCES AND METHOD FOR	)	
DECOMPOSING ORGANIC	)	
HALIDES BY USE THEREOF	)	

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to the first Official Action, please amend the above-identified patent application as follows:

**IN THE CLAIMS:**

Kindly amend claims 4-6, 8, and 10 as follows:

4. (Amended) A catalyst as claimed in claim 2 wherein the oxide is titanium dioxide.

5. (Amended) A catalyst as claimed in claim 2 wherein the sulfate is barium sulfate.

6. (Amended) A catalyst as claimed in claim 1 wherein the organic halide(s) is at least one of chlorodioxins and polychlorodioxins; polychlorobiphenyls; chloroalkanes and polychloroalkanes; chloroalkenes and polychloroalkenes; bromodioxins and polybromodioxins; polybromobiphenyls; bromoalkanes and polybromoalkanes; and bromoalkenes and polybromoalkenes.

8. (Amended) A method of decomposing organic halide(s) in a gas characterized by contacting a gas containing an organic halide(s) with the catalyst described in claim 1 to decompose the organic halide(s).

10. (Amended) A method of decomposing as claimed in claim 8 wherein the organic halide(s) is at least one of chlorodioxins and polychlorodioxins; polychlorobiphenyls; chloroalkanes and polychloroalkanes; chloroalkenes and polychloroalkenes; bromodioxins and polybromodioxins; polybromobiphenyls; bromoalkanes and polybromoalkanes; and bromoalkenes and polybromoalkenes.

**REMARKS**

By the present Preliminary Amendment, all multiple dependency has been eliminated from the original claims. It is to be understood that the revisions to the claims are solely for formalistic purposes and not with regard to patentability and that applicants reserve the right to pursue claims directed to other aspects of the invention encompassed by the original multiple dependent claims or described in the specification.

Entry of the instant Preliminary Amendment and favorable consideration on the merits are respectfully requested.

Should the Examiner have any questions concerning the subject application, the Examiner is invited to contact the undersigned attorney at the number provided below.

Respectfully submitted,

BURNS, DOANE, SWECKER & MATHIS, L.L.P.

By: Robert G. Mukai  
Robert G. Mukai  
Registration No. 28,531

P.O. Box 1404  
Alexandria, Virginia 22313-1404  
(703) 836-6620

Date: March 29, 2002

**Attachment to Preliminary Amendment dated March 29, 2002**

**Marked-up Claims 4-6, 8 and 10**

4. A catalyst as claimed in claim 2 [or 3] wherein the oxide is titanium dioxide.
5. A catalyst as claimed in claim 2 [any one of claims 2 to 4] wherein the sulfate is barium sulfate.
6. A catalyst as claimed in claim 1 [any one of claims 1 to 5] wherein the organic halide(s) is at least one of chlorodioxins and polychlorodioxins; polychlorobiphenyls; chloroalkanes and polychloroalkanes; chloroalkenes and polychloroalkenes; bromodioxins and polybromodioxins; polybromobiphenyls; bromoalkanes and polybromoalkanes; and bromoalkenes and polybromoalkenes.
8. A method of decomposing organic halide(s) in a gas characterized by contacting a gas containing an organic halide(s) with the catalyst described in claim 1 [any one of claims 1 to 5] to decompose the organic halide(s).
10. A method of decomposing as claimed in claim 8 [any one of claims 8 and 9] wherein the organic halide(s) is at least one of chlorodioxins and polychlorodioxins; polychlorobiphenyls; chloroalkanes and polychloroalkanes; chloroalkenes and polychloroalkenes; bromodioxins and polybromodioxins; polybromobiphenyls; bromoalkanes and polybromoalkanes; and bromoalkenes and polybromoalkenes.

## DESCRIPTION

Catalyst for Decomposing Organic Harmful Substances and  
Method for Decomposing Organic Halides by Use Thereof

## Technical field

The present invention relates to a catalyst for decomposing organic harmful substances such as organic halides. More specifically, the present invention relates to a catalyst for decomposing harmful organic halides including dioxins in an exhaust gas generated with burning of urban garbage or industrial waste; or a treatment of plastic materials to make them harmless.

## Background Art

It has been revealed recently that organic harmful substances such as organic halides including dioxins and aromatic chlorides, which are considered to be their precursors, are contained in the gases which were exhausted from the incinerators for burning out urban garbage and industrial waste or the facilities for gasifying and fusing of the urban garbage and industrial waste. In addition, it is pointed out that organic harmful substances including bromodioxins and polybromodioxins are contained in the exhaust gases through thermal treatment of plastic materials used in home electric appliances waste. Regarding the organic halides, although each of the compounds have different toxicities, they are strongly toxic in general, and in

particular dioxins are considered to be deadly poisonous which can strikingly affect the human body, animals and plants by causing deformity or disturbing effects of hormones.

Therefore, the pollution of the environment becomes now a social problem and reduction of the content of organic halides in the exhaust gases from the burning treatment has been urgently required. At present, as removing methods of organic halides including dioxins, various methods such as absorption method using an activated carbon, a thermolysis method or a contact decomposing method using a catalyst are proposed. Among them, the contact decomposing method has excellent characteristics in that it can avoid resynthesis of dioxins because the dioxins can be decomposed under a lower temperature condition below 300°C; and that, since it does not require the secondary treatment which is required in the absorption method and the like, the running cost is low.

As a catalyst used in the above described contact decomposing method, various metal oxides such as vanadium pentaoxide and titanium dioxide; carbonates; and silicates are known as described in Japanese Patent Publication No.38863/94. They are, however, not practical, because they require a high temperature for decomposition and long residence time from several minutes to several hours. Vanadium pentaoxide-titanium dioxide catalysts are disclosed in Japanese Patent Laid-Open No.144117/31 and Japanese Patent Laid-Open No.117557/96. However, when SO<sub>2</sub> is included in the gas to be treated or when SO<sub>2</sub> generates through the decomposition treatment, the oxidation activity of SO<sub>2</sub> become



higher in the use of the catalysts containing vanadium pentaoxide. As a result, there is a problem that a large amount of  $\text{SO}_3$  is produced when these catalysts are applied for purification of the exhaust gases containing  $\text{SO}_x$  besides  $\text{NO}_x$ .

There is the other problem that reduction of the catalytic activity occurs according to the time progress in their uses. The following reasons for this activity reduction can be mentioned:

1. Regarding the method of reducing a substance to be treated in the presence of a catalyst by using ammonia as a reducing agent, the catalytic activity decreases by accumulation of ammonium salts of sulfur such as ammonium bisulfate on the catalyst surface, which is formed by reaction of ammonia and  $\text{SO}_3$  generated as above.

2. There is a further problem that since the oxidizing activity of  $\text{SO}_2$  increases, vanadium pentaoxide is reduced and transferred to a water-soluble vanadyl sulfate ( $\text{VOSO}_4$  having  $\alpha$  type crystals:  $\alpha$ - $\text{VOSO}_4$ ) and, thus, the catalytic activity is reduced according to the time progress in their uses.

3. When chlorides such as  $\text{HCl}$  and  $\text{Cl}_2$  including chlorine gas are included in the gas to be treated or when they are generated through the decomposition process, change in the quality occurs and the catalytic activity are reduced.

To solve these problems, the catalyst in which tin dioxide is contained in the vanadium pentaoxide-titanium dioxide type catalyst as described in Japanese Patent Laid-Open





This vanadyl sulfate (vanadyl sulfate having  $\beta$  type crystals:  $\beta$ -VOSO<sub>4</sub>) is that which per se can be obtained as a crystal having bluish green color. An infrared spectrum provides characteristic peaks at 940 cm<sup>-1</sup> and 510 cm<sup>-1</sup>, respectively, which are not observed in that of the water-soluble vanadyl sulfate (vanadyl sulfate having  $\alpha$  type crystals:  $\alpha$ -VOSO<sub>4</sub>). According to the present invention, a solid vanadyl sulfate containing at least  $\beta$ -VOSO<sub>4</sub> is used. Elution rate in contacting the solid with water is 10% or less than 10%, preferably 5% or less than 5%.

The water-insoluble vanadyl sulfate can be, for example, produced by the following methods:

1. A method comprising adding a reducing agent to vanadium compound of pentavalence in the presence of water to reduce its valence to that less than 5; forming precipitate from a solution obtained by addition of an ammonium salt of sulfuric acid; and calcining the precipitate after drying.

An alternative method comprising forming precipitate from a solution obtained by addition of an ammonium salt of sulfuric acid to a vanadium compound having valence less than 5; and calcining the precipitate after drying.

2. A method comprising adding an ammonium salt of sulfuric acid to vanadyl oxalate and calcining.

3. A method comprising directly calcining vanadyl sulfate.

When a carrier such as silica, alumina, activated carbon and the like, a water insoluble vanadyl in a state where it is immobilized on a carrier can be obtained by impregnating

a solution for forming vanadyl sulfate into the carrier and calcining it. Examples of this solution includes the aqueous solutions before the calcination in the above methods 1 to 3, i. e., an aqueous solution prepared by using a vanadium compound of pentavalence, a reducing substance and an ammonium salt of sulfuric acid; an aqueous solution prepared by using a vanadium compound of a valence less than 5 and an ammonium salt of sulfuric acid; an aqueous solution prepared obtained by using vanadyl oxalate and an ammonium salt of sulfuric acid; and an aqueous solution of vanadyl sulfate.

As the vanadium compound of pentavalence, at least one compound selected from ammonium metavanadate, metavanadic acid, vanadium pentaoxide can be used. Further, as the vanadium compound having a valence less than 5, for example, at least one of vanadium dioxide and vanadium trioxide can be used. Among them, it is the most preferable thing to select ammonium metavanadate as the starting material in the viewpoint of reproducibility of the catalytic effect.

As the reducing agent used in the above method 1, for example, at least one of organic carboxylic acids such as oxalic acid, citric acid and tartaric acid is preferably used.

The water insoluble vanadyl sulfate comprises at least  $\beta$  type crystals ( $\beta$ -VOSO<sub>4</sub>) and is characterized in that it is not dissolved in water and that the vanadium atom under the quadrivalent state has the activity for the decomposition. In this point, this is basically different from the conventional vanadium pentaoxide in the type of the active component, i. e., vanadium atom has the activity under the

- 8 -

pentavalent state. In addition, since the catalyst is water insoluble, it has HCl resistance, and, since it is a sulfate, it has further  $\text{SO}_x$  resistance.

Examples of the ammonium sulfate used in the above methods 1 and 2 include ammonium bisulfate, ammonium sulfite, ammonium sulfate and ammonium persulfate. Among them, ammonium sulfate is preferably because it is inexpensive and it enables to prepare the catalyst to be obtained more easily.

This water insoluble vanadyl sulfate can be used alone as a catalyst for decomposition of an organic compound(s), in particular an organic halide(s).

A complex catalyst can be alternatively obtained by combining this water insoluble vanadyl sulfate with an oxide(s) and a sulfate(s).

This complex catalyst can be obtained the methods such as the following ones:

A. A method comprising mixing the water insoluble vanadyl sulfate, an oxide(s) and a sulfate(s).

B. A method comprising impregnating an aqueous solution for preparation of the water insoluble vanadyl sulfate into a solid mixture of an oxide(s) and a sulfate(s); and calcining the mixture after drying.

C. A method comprising adding an oxide(s) and a sulfate(s) into an aqueous solution for preparation of the vanadyl sulfate to obtain a slurry; and calcining the slurry thus obtained after drying.

As the aqueous solutions for preparation of the water insoluble vanadyl sulfate used in the methods B and C, the

As the oxide, which is combined with the water insoluble vanadyl sulfate, for example, at least one of the oxides, which have one atom(s) selected from the group consisting titanium, zirconium, niobium, molybdenum, tungsten and chromium, can be used. Among them, niobium pentoxide and titanium dioxide are useful and the most preferable one is titanium dioxide.

The other oxides may be produced by an ordinary method such as the nitrate method, the sulfate method and the chloride method.

It is considered to plan by using such oxide(s) to further improve resistance against HCl and SO<sub>x</sub>, as well as the activity based on high dispersion of the vanadyl sulfate as the active component in the catalyst.

As the above sulfate combined with the water insoluble vanadyl sulfate, one or more sulfates selected from sulfates of alkaline earth metals and lead sulfate can be used. As the alkaline earth metals, calcium, barium, strontium or magnesium can be used. Among them, barium is most preferable. Although the production method of barium sulfate is not limited, those produced by the precipitation method and baryta powder obtained by grinding baryta in a machine, for example, may be used. It is considered to plan by this combination of this sulfate to further improve strength of the catalyst formed in a from, and resistance against SO<sub>x</sub>.

As the composite ratio of the above three components, that of the water insoluble vanadyl sulfate may be selected from the range of 0.5 to 100 wt.%, preferably 1 to 30 wt.%, especially preferably 5 to 20 wt.%; that of the oxide(s) may be selected from the range of 0 to 70 wt.%, preferably 20 to 50 wt.%; that of the sulfate(s) may be selected from the range of 0 to 70 wt.%, preferably 20 to 50 wt.%.

The temperature for calcining to form the water insoluble vanadyl sulfate may be that at which the insoluble vanadyl sulfate can be made. There is a tendency that calcination at a lower temperature results in decline of convert efficiency into the water insoluble vanadyl sulfate, while calcination at a higher temperature results in decomposition of the water



insoluble vanadyl sulfate thus formed. Therefore, the calcination temperature may be selected from the range from 250°C to 500°C, preferably 300°C to 450°C.

As noted above, according to the catalyst of the present invention, the water insoluble vanadyl sulfate alone may be used, in the condition where it can be optionally carried on a publicly-known carrier; and a complex catalyst by combination of the above specific oxide(s) and sulfate(s) with the water insoluble vanadyl sulfate may be used, in a condition where it may be optionally carried on a publicly-known carrier. Excellent properties such as the catalytic activity, durability and forming property can be further obtained by forming such complex catalyst.

The catalyst may be used in a desired shape for decomposition reaction. For example, it may be used in a form such as pellet, sphere, granule, plate, honeycomb or three-dimensional net forms. The size as the pellet form, for example, its diameter may be from 1 mm to 50 mm and its length may be 5 mm to 60 mm. The diameter in the sphere form may be for example in the range 1 mm to 50 mm. The size in the granule form may be from 1 to 40 mesh. When it is formed in a plate, honeycomb or three-dimensional net form, more preferable effects can be obtained by forming it in a size so that its cell number per one inch-square can reach to from 5 to 400.

Such forms can be obtained, for example, by forming a precursor of the catalyst before calcining; or a catalyst powder after calcining according to an ordinary method. When

the oxide(s) and the sulfate(s) are used as a carrier for forming and the water insoluble vanadyl sulfate is carried on this carrier, a complex catalyst in a desired shape can be obtained by forming the carrier per se in the desired form.

When it is necessary to reinforce the mechanical strength of the catalyst depending on its shape, an additive(s) such as whisker, fibers, clay or binders, which has used for catalyst formation, may be used optionally if required. When the catalyst is coated on a desired carrier of the desired shape such as sphere, plate or honeycomb, or when the catalyst is baked for calcination on such carrier, the catalyst of the desired shape can be obtained by forming the carrier per se in the desired form.

The smaller size (when the pellet, sphere or granule form is used) and the greater cell number (when the plate, honeycomb or three-dimensional net form) are preferable, because the total surfaces become greater. Regarding the cases that pressure loss of the gas to be conducted becomes greater and that blocking by dust can easily occur, the above sizes are preferable.

The target to be decomposed can be efficiently decomposed by contacting the catalyst obtained as noted above with a gas including an organic halide(s) as the target to be decomposed. As this gas including the organic halide(s), exhaust gases by incinerating garbage or burning industrial waste can be mentioned.

Examples of the organic halide(s) as the substances to be decomposed include organic chlorine hydrocarbons and

organic bromine hydrocarbons. The organic chlorine hydrocarbons include chlorodioxins and polychlorodioxins; polychlorobiphenyls; chloroalkanes and polychloroalkanes such as chlorobenzene, dichlorobenzene, chlorotoluene, chlorophenol and chloromethane; chloroalkenes and polychloroalkenes such as chloroethylene. The organic bromine hydrocarbons include bromodioxins and polybromodioxins; polybromobiphenyls; bromoalkanes and polybromoalkanes such as bromobenzene, dibromobenzene, bromotoluene, bromophenol, polybromobiphenyl ether, bromomethane; bromoalkenes and polybromoalkenes such as bromoethylene. The catalyst according to the present invention can be effectively used against a gas comprising at least one compound of the above compounds.

The temperature for the contact of the catalyst and the substance to be treated is preferably in the range from 140°C to 300°C. When the reaction temperature is lower than 140°C, there is a case that the activity becomes lower owing to high absorption of the organic halide(s). When the temperature is higher than 300°C, there is a case that resynthesis of dioxins can occur from the decomposition products in the dioxin decomposition.

Regarding the activity and the cost for decomposition treatment, the space velocity may be selected from the range of 1,000 to 20,000 h<sup>-1</sup> to obtain preferable effects. Further, the most preferable one is in the range from 2,000 to 7,000 h<sup>-1</sup>.

- 14 -

The decomposition treatment can be carried out at an oxygen concentration in the range from 1 to 99%, preferably from 5 to 30%.

Since the catalyst according to the present invention has an excellent resistance against  $\text{SO}_x$ , it is especially suitable in the case when the gas to be treated includes  $\text{SO}_x$  ( $x=1.5$  to  $3.0$ , for example) per se, or components which generate  $\text{SO}_x$  during the heating treatment for decomposition.

As the equipments for decomposition using the catalyst according to the present invention, those having a structure may be used, which comprises a decomposition area capable of maintaining the catalyst; a means for introducing a gas to be treated into the decomposition area; a means for contacting the gas thus introduced with the catalyst; a means for exhausting a gas including the decomposition products thus formed by the action of the catalyst from the decomposition area. The exhaust gas after the decomposition treatment may be optionally subjected to various treatments if required.

Since the catalysts of the present invention hold excellent activity and durability, a continuous operation for long time can be carried out and the decomposition efficiency can be greatly improved.

#### [Examples]

Hereinafter, although the present invention will be more specifically described by Examples and Comparative Examples, the present invention is not limited to them.

Examples 1 to 21 and Comparative Examples 1 to 22

#### Examples for Catalyst Production

(Catalyst A)

Ammonium metavanadate (50g) was added to water to dissolve it by heating at 80°C and 125g of oxalic acid was added under stirring to reduce vanadium. Then, 57g of ammonium sulfate was added into this solution containing vanadium and 510g of the anatase-type of titanium dioxide and 260g of barium sulfate were added one by one. The obtained slurry solution was dried with a spray dry to give powder. A small amount of water was added to the obtained powder and the mixture was kneaded and molded by extruding in pellets of 3 mm  $\phi$  and 3 mm in length by an extruder. After drying the obtained pellets again, these were baked at 430°C to obtain the catalyst A comprising 9 wt.% of a water-insoluble vanadyl sulfate ( $\beta$ -VOSO<sub>4</sub>), 59 wt.% of titanium dioxide and 32 wt.% of barium sulfate.

(Catalyst B)

Catalyst B was obtained in the same manner as that for catalyst A except that the pellet size was changed to 1.6 mm  $\phi$  and 3 mm in length.

(Catalyst C)

Catalyst C was obtained in granules of 10-20 mesh by grinding Catalyst A.

(Catalyst D)

Catalyst A was crushed and a honeycomb catalyst of the cell number of 35 per square inch was prepared by using the crushed materials thus obtained according to an ordinary method and a piece of 12 mm width and 18 cm length was cut out to obtain Catalyst D.

(Catalyst E)

Catalyst D was obtained in the same manner as that for Catalyst A except that niobium pentaoxide was used for the anatase-type of titanium dioxide. Catalyst D comprised 9 wt.% of a water-insoluble vanadyl sulfate ( $\beta$ -VOSO<sub>4</sub>), 59 wt.% of niobium pentaoxide and 32 wt.% barium sulfate.

(Catalyst F)

Catalyst F was obtained in the same manner as that for Catalyst A except that the anatase-type of titanium dioxide and barium sulfate were not used.

(Catalyst G)

Ammonium metavanadate (100g) was added to water to dissolve it by heating at 80°C and 103g of ammonium paratungstate was added under stirring to be dissolved. The anatase-type of titanium dioxide (700g) was added to this solution to prepare the slurry solution. The obtained slurry solution was dried with a spray dry to give powder. A small amount of water was added to the obtained powder and the mixture was kneaded and molded by extruding in pellets of 3 mm  $\phi$  and 3 mm in length by an extruder. After drying the obtained pellets again, they were baked at 500°C to obtain the catalyst G comprising 9 wt.% of vanadium pentaoxide, 10 wt.% of tungsten trioxide and 81 wt.% of titanium dioxide.

(Catalyst H)

Catalyst H was obtained in granules by crushing Catalyst G in 10-20 mesh.

(Catalyst I)

Catalyst G was crushed and a honeycomb catalyst of the cell number of 35 per square inch was prepared by using the crushed materials according to an ordinary method and a piece of 12 mm width and 18 cm length was cut out to obtain Catalyst I.

(Catalyst J)

Ammonium metavanadate (100g) was added to water to dissolve it by heating at 80°C and 510g of the anatase-type of titanium dioxide and 276g of barium sulfate were added to this solution to prepare the slurry solution. The obtained slurry solution was dried with a spray dry to give powder. A small amount of water was added to the obtained powder and the mixture was kneaded and molded by extruding in pellets of 3 mm  $\phi$  and 3 mm in length by an extruder. After drying the obtained pellets again, they were baked at 500°C to obtain the catalyst J comprising 9 wt.% of vanadium pentaoxide, 59 wt.% of tungsten trioxide and 32 wt.% of titanium dioxide.

(Catalyst K)

Catalyst K was obtained in granules by crushing Catalyst J in 10-20 mesh.

(Catalyst L)

A catalyst was prepared from titanium dioxide in order to confirm whether titanium dioxide has catalytic effect. In particular, a slurry solution obtained by adding 500g of the anatase-type of titanium dioxide to water was dried by a spray dry to obtain powder. A small amount of water was added to the obtained powder and the mixture was kneaded and molded by extruding in pellets of 3 mm  $\phi$  and 3 mm in length

by an extruder. After drying the obtained pellets again, they were baked at 430°C to obtain the catalyst L of the anatase-type of titanium dioxide.

#### Test Examples

Using the above catalysts, the following tests were carried out:

##### 1. MCB decomposition activity test 1

MCB (monochlorobenzene) decomposition activity tests were carried out using catalysts A, E, F, H and J individually. A catalyst was charged in a cylindrical glass reactor of 30 mmφ to occupy the volume of 10 ml. A gas having a composition of 10 volume % oxygen and 90 volume % nitrogen containing 16 ppm MCB was allowed to continuously flow and the decomposition reaction was carried out at 6,000 hr<sup>-1</sup> of the space velocity and at a reaction temperature between 140°C and 180°C for 5 hours. Data by the reaction for 5 hours are shown in Table 1. The decomposition rate (%) by gas chromatographic analysis was calculated according to the equation: ((MCB concentration at the inlet) - (MCB concentration at the outlet) / (MCB concentration at the inlet) × 100).

Catalysts A, E and F exhibited higher decomposition rates in comparison with Catalysts G, J and L.



[Table 1]

	Catalyst	Reaction Temperature (°C)	MCB Decomposition Rate (%)
Example 1	A	180	99.9
Example 2	A	160	99.5
Example 3	A	140	99.0
Example 4	E	180	98.4
Example 5	E	160	98.1
Example 6	E	140	97.5
Example 7	F	180	95.8
Example 8	F	160	95.4
Example 9	F	140	94.0
Comparative Example 1	G	180	86.7
Comparative Example 2	G	160	82.5
Comparative Example 3	G	140	78.1
Comparative Example 4	J	180	85.2
Comparative Example 5	J	160	80.9
Comparative Example 6	J	140	76.5
Comparative Example 7	L	200	0.1
Comparative Example 8	L	180	0.0

## 2) MCB Decomposition activity test 2

Catalyst D or I in the form of a honeycomb shape of 12 mm square section and 18 cm length was filled in a stainless steel (SUS) reactor having a 13 mm square section. A gas having a composition of 10 volume % oxygen and 90 volume % nitrogen containing 16 ppm MCB was allowed to continuously

flow and the composition reaction was carried out for 5 hours at 7,000 hr<sup>-1</sup> of the space velocity and at the reaction temperature of 200°C. Data for the 5-hour reaction are exhibited in Table 2. The decomposition rate was obtained in the same manner as that in MCB decomposition activity test 1.

[Table 2]

	Catalyst	Reaction Temperature (°C)	MCB Decomposition Rate (%)
Example 10	D	200	90.9
Comparative Example 9	I	200	80.8

### 3) Decomposition activity test against DXNs

DXNs (dioxins) decomposition activity test was carried out using Catalysts A, B and G, individually. A catalyst was filled in a cylindrical SUS reactor having a 29 mm square section to occupy a volume of 60 ml. A gas having the composition of 10 volume % oxygen, 80 volume % nitrogen and 10 volume % steam containing dioxins (2378-T4CDD, 123678-H6CDD and 08CDD) so that the inlet concentration was controlled as shown in Table 3 was allowed to continuously flow and decomposition reaction was carried out at 10,000 hr<sup>-1</sup> of the space velocity at a temperature between 140°C and 180°C for 300 hours. Data during the reaction between 200 to 300 hours are shown in Table 3. The decomposition rate

(%) was calculated according to the equation:  $((\text{DXNs concentration at the inlet}) - (\text{DXNs concentration at the outlet}) / (\text{DXNs concentration at the inlet}) \times 100)$ .

[Table 3]

	Catalyst	Reaction Temp. (°C)	Inlet conc. ngTEQ/Nm <sup>3</sup> h	Outlet Conc. ngTEQ/Nm <sup>3</sup> h	DXNs Decomposition Rate (%)
Example 11	A	160	12.0	0.177	98.5
Example 12	A	140	12.0	0.202	98.3
Example 13	B	140	12.0	0.032	99.7
Comparative Example 10	G	180	9.8	0.739	92.8
Comparative Example 11	G	160	9.8	0.911	90.7
Comparative Example 12	G	140	9.8	1.20	87.8

#### 4) Test of HCl resistance

To confirm influence by difference of HCl amounts generated during decomposing, Catalyst C, H or K was charged in a cylindrical glass reactor of 12 mm  $\phi$  to occupy the volume of 5 ml. Each gas composed of 10 volume % oxygen, and 90 volume % nitrogen containing 100 ppm or 16 ppm MCB was allowed to continuously flow to decompose them at 3,000 hr<sup>-1</sup> of the space velocity and at 180°C of the reaction temperature to confirm a tendency of time-lapse degradation. The decomposition rate (%) was calculated in the same manner as

in that of MCB decomposition activity test 1. The results thus obtained are shown in Table 4

[Table 4]

Passage Time (hr.)	MCB Concentration at the Inlet: 100 ppm			MCB Concentration at the Inlet: 16 ppm		
	Example 14	Compa-rative Example 13	Compa-rative Example 14	Example 14	Compa-rative Example 15	Compa-rative Example 16
	Catalyst C	Catalyst H	Catalyst K	Catalyst C	Catalyst H	Catalyst K
1	99.3 (99.3)	16.0 (16.0)	34.5 (34.5)	99.7 (16.0)	85.2 (13.6)	86.5 (13.8)
25	94.3 (94.3)	49.0 (49.0)	51.1 (51.1)	99.9 (16.0)	84.2 (13.5)	85.9 (13.7)
50	92.0 (92.0)	52.9 (52.9)	53.2 (53.2)	99.8 (16.0)	83.8 (13.5)	85.2 (13.6)
76	91.1 (91.1)	52.3 (52.3)	53.5 (53.5)	99.8 (16.0)	83.6 (13.4)	84.8 (13.6)
100	91.4 (91.4)	46.9 (46.9)	52.9 (52.9)	99.4 (15.9)	83.1 (13.3)	84.6 (13.5)
125	90.8 (90.8)	50.2 (50.2)	53.7 (53.7)	-	-	-
150	91.0 (91.0)	52.3 (52.3)	53.9 (53.9)	-	-	-
175	90.6 (90.6)	50.9 (50.9)	53.5 (53.5)	-	-	-

The number in each pair of the blackest means the HCl amount thus formed (ppm) based on the MCB decomposition.

5) Oxidation activity test on SO<sub>2</sub>

Catalyst A, G or J was charged in a cylindrical glass reactor of 30 mm  $\phi$  to occupy a volume of 10ml. A gas has a composition of 10 volume % oxygen, 79.9 volume % nitrogen and 10 volume % steam containing 0.1 volume % sulfur dioxide was allowed to continuously flow and their reaction was carried out at 5,000 hr<sup>-1</sup> of the space velocity at a reaction temperature between 140°C to 180°C for 5 hours. Data after 5 hours are shown in Table 5. The oxidation rate (%) of sulfur dioxide was calculated by the equation, ((SO<sub>2</sub> concentration at the inlet) - (SO<sub>2</sub> concentration at the outlet) / (SO<sub>2</sub> concentration at the inlet)  $\times$  100).

[Table 5]

	Catalyst	Reaction Temperature (°C)	Oxidation Rate of SO <sub>2</sub> (%)
Example 16	A	180	0.4
Example 17	A	160	0.0
Example 18	A	140	0.0
Comparative Example 17	G	180	2.5
Comparative Example 18	G	160	1.6
Comparative Example 19	G	140	1.2
Comparative Example 20	J	180	3.3
Comparative Example 21	J	160	2.4
Comparative Example 22	J	140	1.8

6) Decomposition activity test on bromobenzene

Catalyst A or G was charged in a cylindrical glass reactor of 30 mm  $\phi$  to occupy a volume of 10 ml. A gas having a composition of 10 volume % oxygen and 90 volume % nitrogen containing



[Table 6]

	Catalyst	Reaction Temperature (°C)	Decomposition Rate of MBB(%)
Example 19	A	180	98.8
Example 20	A	160	98.5
Example 21	A	140	98.1
Comparative Example 23	G	180	85.5
Comparative Example 24	G	160	80.8
Comparative Example 25	G	140	77.2

#### Industrial Applicability

According to the present invention, a catalyst can be provided at a low cost by which a higher activity and durability of the catalyst can be obtained in the purification method of a gas containing an organic chlorine compound(s) such as dioxin(s) as noted above. Further, according to the present invention, a method of decomposing an organic halide(s) in a high efficient by using the catalyst.



In particular, the catalyst according to the present invention is excellent not only in its activity, durability and SO<sub>2</sub> resistance for decomposition of an organic halide(s), but also in substantially no oxidization of SO<sub>2</sub> to SO<sub>3</sub> as well as in that it is HCl resistant. Therefore, it is suitably used for highly efficient decomposition of the organic halide(s) in the cases that dust is coexist; the gas to be treated contains SO<sub>x</sub> or HCl; or they generate in the decomposition area.

## CLAIMS

1. A catalyst for decomposing an organic halide(s) characterized in comprising a water-insoluble vanadyl sulfate ( $\beta$ -VOSO<sub>4</sub>).

2. A catalyst as claimed in claim 1 wherein the catalyst further contain at least one oxide comprising an atom(s) selected from the group consisting of titanium, zirconium, niobium, molybdenum, tungsten and chromium; and at least one sulfate comprising an atom(s) selected from the group consisting of alkaline earth metals and lead.

3. A catalyst as claimed in claim 2 wherein 0 to 70 wt.% of the oxide(s), 0 to 70 wt.% of the sulfate(s) and 0.5 to 100 wt.% of the water-insoluble vanadyl sulfate are included.

4. A catalyst as claimed in claim 2 or 3 wherein the oxide is titanium dioxide.

5. A catalyst as claimed in any one of claims 2 to 4 wherein the sulfate is barium sulfate.

6. A catalyst as claimed in any one of claims 1 to 5 wherein the organic halide(s) is at least one of chlorodioxins and polychlorodioxins; polychlorobiphenyls; chloroalkanes and polychloroalkanes; chloroalkenes and polychloroalkenes; bromodioxins and polybromodioxins; polybromobiphenyls; bromoalkanes and polybromoalkanes; and bromoalkenes and polybromoalkenes.

7. A catalyst as claimed in claim 6 wherein the organic halide(s) is at least one of chlorodioxins and

polychlorodioxins, polychlorobiphenyls, chlorobenzene, dichlorobenzene, chlorotoluene, chlorophenol, chloromethane, chloroethylene, bromodioxins and polybromodioxins, polybromobiphenyls, bromobenzene, dibromobenzene, bromotoluene, bromophenol, polybromobiphenyl ether, bromomethane and bromoethylene.

8. A method of decomposing organic halide(s) in a gas characterized by contacting a gas containing an organic halide(s) with the catalyst described in any one of claims 1 to 5 to decompose the organic halide(s).

9. A method of decomposing as claimed in claim 8 wherein the contact between the organic halide(s) and the catalyst is carried out at a temperature from 140 to 300 °C.

10. A method of decomposing as claimed in any one of claims 8 and 9 wherein the organic halide(s) is at least one of chlorodioxins and polychlorodioxins; polychlorobiphenyls; chloroalkanes and polychloroalkanes; chloroalkenes and polychloroalkenes; bromodioxins and polybromodioxins; polybromobiphenyls; bromoalkanes and polybromoalkanes; and bromoalkenes and polybromoalkenes.

11. A method of decomposing as claimed in claim 10 wherein the organic halide(s) is at least one of chlorodioxins and polychlorodioxins, polychlorobiphenyls, chlorobenzene, dichlorobenzene, chlorotoluene, chlorophenol, chloromethane, chloroethylene, bromodioxins and polybromodioxins, polybromobiphenyls, bromobenzene, dibromobenzene, bromotoluene, bromophenol, polybromobiphenyl ether, bromomethane and bromoethylene.

# ABSTRACT

A catalyst of a water insoluble vanadyl sulfate or a complex catalyst, in which a specific oxide and a specific sulfate are combined to the water insoluble vanadyl sulfate are excellent not only in their activity, durability and SO<sub>2</sub> resistance, not only in substantially no oxidization of SO<sub>2</sub> to SO<sub>3</sub> as well as in HCl resistant. Therefore, using this catalyst, a decomposition treatment of an organic halide(s) can be carried out with high efficiency and good stability. In particular, a efficient decomposition treatment of an organic halide(s) can be carried out also in the cases that dust is coexist; the gas to be treated contains SO<sub>x</sub> or HCl; or they generate in the decomposition area.

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**  
(Includes Reference to Provisional and PCT International Applications)

ATTORNEY'S DOCKET NUMBER

029430-507

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Catalyst for Decomposing Organic Harmful Substances and Method for

Decomposing Organic Halides by Use Thereof

the specification of which (check only one item below):

☒ is attached hereto.

☐ was filed as United States application

Number \_\_\_\_\_

on \_\_\_\_\_

and was amended

on \_\_\_\_\_ (if applicable).

☒ was filed as PCT international application

Number PCT/JP00/06635

on September 27, 2000

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(e) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

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COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. §119
Japan	11-276217	29.09.1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
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**PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:**

**U.S. APPLICATIONS**

**STATUS (check one)**

U.S. APPLICATION NUMBER

U.S. FILING DATE

PATENTED

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**PCT APPLICATIONS DESIGNATING THE U.S.**

PCT APPLICATION NO.

PCT FILING DATE

U.S. APPLICATION NUMBERS  
ASSIGNED (if any)

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William L. Mathis	17,337	Ralph L. Freeland, Jr.	16,110	William C. Rowland	30,888
Peter H. Smolka	15,913	Robert G. Mukai	28,531	T. Gene Dillahunt	25,423
Robert S. Swecker	19,885	George A. Hovanec, Jr.	28,223	Anthony W. Shaw	30,104
Platon N. Mandros	22,124	James A. LaBarre	28,632	Patrick C. Keane	32,858
Benton S. Duffett, Jr.	22,030	E. Joseph Gess	28,510	Bruce J. Boggs, Jr.	32,344
Joseph R. Magnone	24,239	R. Danny Huntington	27,903	William H. Benz	25,952
Norman H. Stepno	22,716	Eric H. Weisblatt	30,505	Peter K. Skiff	31,917
Ronald L. Grudziecki	24,970	James W. Peterson	26,057	Richard J. McGrath	29,195
Frederick G. Michaud, Jr.	26,003	Teresa Stanek Rea	30,427	Matthew L. Schneider	32,814
Alan E. Kopecki	25,813	Robert E. Krebs	25,885	Michael G. Savage	32,596
Regis E. Slutter	26,999	Robert M. Schulman	31,196	Gerald F. Swiss	30,113
Samuel C. Miller, III	27,360				

and: \_\_\_\_\_

Address all correspondence to:

Robert G. Mukai  
BURNS, DOANE, SWECKER & MATHIS, L.L.P.  
P.O. Box 1404  
Alexandria, Virginia 22313-1404

Address all telephone calls to: Robert G. Mukai Customer No. 21839 at (703) 836-6620.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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ATTORNEY'S DOCKET NO.

029430-507

FULL NAME OF SOLE OR FIRST INVENTOR

SIGNATURE

DATE  
March 18,  
2002

Isao TAKASU

*Isao Takasu*

RESIDENCE

CITIZENSHIP

Hokkaido, Japan JPX

Japanese

POST OFFICE ADDRESS

11-1-13-102, Kagura 6jyou, Asahikawa-shi, Hokkaido 070-8006; Japan

FULL NAME OF SECOND JOINT INVENTOR, IF ANY

SIGNATURE

DATE  
March 18,  
2002

Kenji FUJITA

*Kenji Fujita*

RESIDENCE

CITIZENSHIP

Tokyo, Japan JPX

Japanese

POST OFFICE ADDRESS

c/o Ube Industries, Ltd.,  
2-1, Shibaura 1-chome, Minato-ku, Tokyo 105-8449, Japan

FULL NAME OF THIRD JOINT INVENTOR, IF ANY

SIGNATURE

DATE

RESIDENCE

CITIZENSHIP

POST OFFICE ADDRESS

FULL NAME OF FOURTH JOINT INVENTOR, IF ANY

SIGNATURE

DATE

RESIDENCE

CITIZENSHIP

POST OFFICE ADDRESS

FULL NAME OF FIFTH JOINT INVENTOR, IF ANY

SIGNATURE

DATE

RESIDENCE

CITIZENSHIP

POST OFFICE ADDRESS

FULL NAME OF SIXTH JOINT INVENTOR, IF ANY

SIGNATURE

DATE

RESIDENCE

CITIZENSHIP

POST OFFICE ADDRESS

FULL NAME OF SEVENTH JOINT INVENTOR, IF ANY

SIGNATURE

DATE

RESIDENCE

CITIZENSHIP

POST OFFICE ADDRESS

FULL NAME OF EIGHTH JOINT INVENTOR, IF ANY

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DATE

RESIDENCE

CITIZENSHIP

POST OFFICE ADDRESS

FULL NAME OF NINTH JOINT INVENTOR, IF ANY

SIGNATURE

DATE

RESIDENCE

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POST OFFICE ADDRESS